



Performance optimum analysis of an irreversible molten carbonate fuel cell–Stirling heat engine hybrid system



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ABSTRACT

A new hybrid system mainly consists of a molten carbonate fuel cell (MCFC) and a Stirling heat engine is established, where the Stirling heat engine is driven by the high-quality waste heat generated in the MCFC. Based on the electrochemistry and non-equilibrium thermodynamics, analytical expressions for the efficiency and power output of the hybrid system are derived by taking various irreversible losses into account. It shows that the performance of the MCFC can be greatly enhanced by coupling a Stirling heat engine to further convert the waste heat for power generation. By employing numerical calculations, not only the influences of multiple irreversible losses on the performance of the hybrid system are analyzed, but also the impacts of some operating conditions such as the operating temperature, input gas compositions and operating pressure on the performance of the hybrid system are also discussed. The investigation method in the present paper is feasible for some other similar energy conversion systems as well.

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1. Introduction

Due to the rising fuel prices, growing environmental concerns, and existing and upcoming environmental regulations, there is a growing pressure on power generation to operate in a more efficient, cost-effective and environment-friendly way. Because of their high efficiency and zero toxic emission levels, fuel cells are considered as a potential alternative to traditional power plant [1–3]. Among the existing fuel cell technologies [4–6], the molten carbonate fuel cell (MCFC) as a typical high-temperature fuel cell shows a great promise due to its fuel flexibility, high efficiency, and high temperature of the exhaust heat [7–9]. The high quality of the waste heat allows favorable co-generation and combination with other types of power generators such as heat engines and micro gas turbines [10–13].

Since it is difficult to experimentally quantify the interrelated parameters governing a hybrid system, theoretical modeling and numerical analysis become essential for the optimization of the system design and operating conditions. A number of numerical

modeling investigations have been carried out about the MCFC-based hybrid system [12–17]. Some scholars theoretically simulated various MCFC–heat engine hybrid systems, and the performances of the hybrid systems are evaluated and optimized [5,6,12,13]. Some scholars modeled the MCFC-based hybrid systems for different usages from different viewpoint and different scale level [4,14–17], the obtained results may provide some theoretical basis for the development of practical MCFC-based hybrid systems. Recently, Masoud [18] performed the thermodynamic analysis of SOFC–Stirling hybrid plants using alternative fuels, it is found that the overall power production was increased by approximately 10% compared to that of a stand-alone SOFC plant. Among the numerous bottoming power generators, Stirling heat engine with its incomparable superiority becomes worthy of choice due to its simple construction and its manufacture being the same as the reciprocating internal combustion engine. The Stirling engine would obtain the economy of scale and could be built as a cheap power source [17,18,20]. The direct conversion of waste heat from the MCFC into mechanical power through Stirling heat engine may reduce not only the manufacture cost but also the manufacture complexity.

In the present paper, an irreversible thermodynamic–electrochemical model of a MCFC–Stirling heat engine hybrid system is established, in which not only the irreversible losses in the

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MCFC but also the heat-leak from the fuel cell to the environment as well as heat transfer between the fuel cell and the heat engine are considered. Based on the thermodynamic–electrochemical analysis, new expressions for some key parameters of the hybrid system such as the efficiency and power output are derived, from which the general performance characteristics are revealed and the optimal regions for some important performance parameters are given. The effects of some irreversible losses and operating conditions on the performance of the hybrid system are discussed, and consequently, the performance characteristics of the hybrid system are optimized. The results obtained will be useful in discovering feasible solutions that may lead to a preliminary conceptual design of a MCFC–Stirling heat engine hybrid system.

2. An irreversible model of the MCFC–Stirling heat engine hybrid system

A new hybrid system is considered to be composed of a MCFC, a Stirling heat engine and a regenerator, as shown in Fig. 1. The MCFC in the hybrid system plays a role of the high-temperature heat reservoir of a Stirling engine for a further use of the waste heat. The regenerator acts as a counter-flow heat exchanger, which economically absorbs the heat in the high-temperature exhaust gas to preheat the reactants to attain the reaction temperature.

In order to analyze the performance of the whole hybrid system, the following major assumptions are often adopted [7,8,12,20,21]:

- (1) Both the MCFC and the Stirling engine are operated under steady-state condition;
- (2) Operating temperature and pressure in the MCFC are uniform and kept as constants;
- (3) All gases involved are assumed to be compressible ideal gases;
- (4) Chemical reactions are complete and no reactants are remained after the reactions.

With the help of these assumptions, the expressions of the performance parameters for the hybrid system can be obtained. Below, we will analyze each component in the hybrid system respectively and then study the performance characteristics of the whole hybrid system.

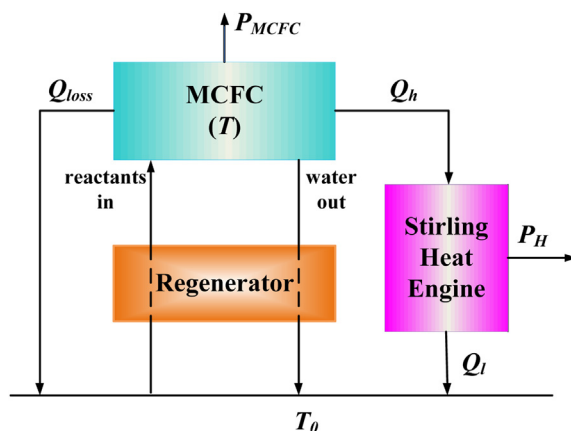


Fig. 1. The schematic diagram of an irreversible MCFC–Stirling heat engine hybrid system.

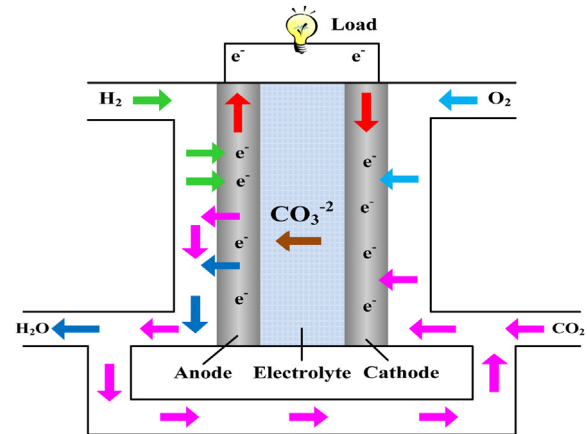
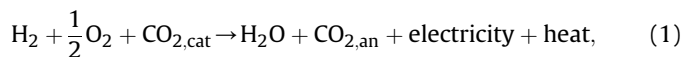


Fig. 2. The schematic diagram of an MCFC [5].

2.1. The MCFC model

The MCFC model presented in this study has been previously reported in Ref. [5]. As shown in Fig. 2, the produced carbon dioxide is transported from the anode to the cathode while the produced carbonate ions flow from cathode to anode. To sustain the total electrochemical reaction, the hydrogen and oxygen are provided continuously to the anode and the cathode, respectively. The overall electrochemical reaction is



where subscripts “an” and “cat” indicate, respectively, “anode” and “cathode”. In order to quantitatively describe the electrochemical reactions in the MCFC, it is quite important to understand the thermodynamic operation principles of the fuel cell. The basic thermodynamic relationship can be given as [5,12]

$$-\Delta\dot{H} = -\frac{\Delta h}{n_e F} j A, \quad (2)$$

where n_e is the number of electrons, F is Faraday's constant, j is the current density, A is the polar plate area of the MCFC, Δh is the molar enthalpy change and can be calculated from the data in Table 1 [5]. According to the basic thermodynamic relationship: $-\Delta H = -\Delta G - T\Delta S$, the total energy ($-\Delta H$) can be divided into two parts, i.e., ($-\Delta G$) and ($-T\Delta S$), which are representative of electrical energy and thermal energy, respectively. As long as the enthalpy change is more negative than the Gibbs free energy change of the reaction, a part of the total energy, which cannot be converted to electrical energy, will be released as heat.

Through agglomerate model developed by Yuh and Selman [21], the power output and efficiency of the MCFC system can be, respectively, expressed as [5]

Table 1
Thermodynamic parameters for the reactants/product at 1 atm, where (g) and (l) refer to gas and liquid phases, respectively.

Compound	$g(T_0)$ (J mol ^{−1})	L_v (J mol ^{−1})	Heat capacity
H ₂ (g)	−38,960	—	$27.28 + 0.00326T + 50,000/T^2$
O ₂ (g)	−61,120	—	$29.96 + 0.00418T - 167,000/T^2$
H ₂ O (g)	−298,130	—	$30.00 + 0.01071T + 33,000/T^2$
H ₂ O (l)	−306,690	40,700	75.44

$$\begin{aligned}
P_{\text{cell}} &= U_{\text{cell}} j A \\
&= \left\{ E_0 + \frac{RT}{n_e F} \ln \left[\frac{p_{\text{H}_2, \text{an}} (p_{\text{O}_2, \text{cat}})^{1/2} p_{\text{CO}_2, \text{cat}}}{p_{\text{H}_2\text{O}, \text{an}} p_{\text{CO}_2, \text{an}}} \right] - 2.27 \right. \\
&\quad \times 10^{-9} j \exp \left(\frac{E_{\text{act}, \text{an}}}{RT} \right) p_{\text{H}_2, \text{an}}^{-0.42} p_{\text{CO}_2, \text{an}}^{-0.17} p_{\text{H}_2\text{O}, \text{an}}^{-1.0} - 7.505 \\
&\quad \times 10^{-10} j \exp \left(\frac{E_{\text{act}, \text{cat}}}{RT} \right) p_{\text{O}_2, \text{cat}}^{-0.43} p_{\text{CO}_2, \text{cat}}^{-0.09} - 0.5 \\
&\quad \left. \times 10^{-4} j \exp \left[3016 \left(\frac{1}{T} - \frac{1}{923} \right) \right] \right\} j A \quad (3)
\end{aligned}$$

and

$$\begin{aligned}
\eta_{\text{cell}} &= \frac{P_{\text{cell}}}{-\Delta \dot{H}} \\
&= -\frac{n_e F}{\Delta h} \left\{ E_0 + \frac{RT}{n_e F} \ln \left[\frac{p_{\text{H}_2, \text{an}} (p_{\text{O}_2, \text{cat}})^{1/2} p_{\text{CO}_2, \text{cat}}}{p_{\text{H}_2\text{O}, \text{an}} p_{\text{CO}_2, \text{an}}} \right] - 2.27 \right. \\
&\quad \times 10^{-9} j \exp \left(\frac{E_{\text{act}, \text{an}}}{RT} \right) p_{\text{H}_2, \text{an}}^{-0.42} p_{\text{CO}_2, \text{an}}^{-0.17} p_{\text{H}_2\text{O}, \text{an}}^{-1.0} - 7.505 \\
&\quad \times 10^{-10} j \exp \left(\frac{E_{\text{act}, \text{cat}}}{RT} \right) p_{\text{O}_2, \text{cat}}^{-0.43} p_{\text{CO}_2, \text{cat}}^{-0.09} - 0.5 \\
&\quad \left. \times 10^{-4} j \exp \left[3016 \left(\frac{1}{T} - \frac{1}{923} \right) \right] \right\}, \quad (4)
\end{aligned}$$

where $E_0 = -\Delta G/(n_e F)$ is the ideal standard potential, $\Delta G = -242,000.0 + 45.8T$ [22]; R is the universal gas constant; E_{act} is the activation energy and the p_k are the partial pressures of species k at the anode or cathode.

2.2. The regenerator

As illustrated in Fig. 1, the regenerator, working as a heat exchanger in the hybrid system, heats the inlet reactants from the ambient temperature to the cell temperature by using the high temperature outlet gas of the fuel cell. Owing to the existence of the thermal resistances, the regenerative losses are inevitable, and it is often assumed that the rate of the regenerative losses is proportional to the temperature difference between the fuel cell and the environment, i.e.,

$$\dot{Q}_{\text{re}} = k_{\text{re}}(1 - \varepsilon)(T - T_0), \quad (5)$$

where k_{re} is a proportional coefficient and ε is the efficiency of the regenerator. With the help of regenerator, the fuel cell and hence the whole hybrid system can be ensured to work normally and continually under the steady-state condition.

2.3. The Stirling heat engine

The Stirling cycle, one of the important standard air cycles for heat engines [10,11], has been seriously considered for a variety of uses. Its main advantages are that the cycle may be driven by a wide variety of fuels, and it offers the opportunity

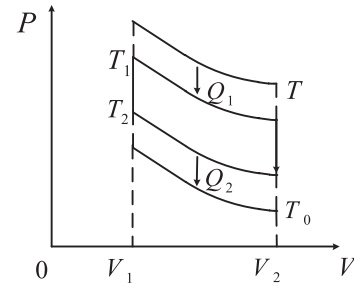


Fig. 3. PV-diagram of a Stirling cycle.

for high efficiency power generation [10,11,23,24]. As shown in Fig. 3, the Stirling cycle is composed of two isothermal processes at temperatures T_1 and T_2 , and two constant-volume processes at volume V_1 and V_2 , respectively. For a practical Stirling heat engine, there are invariably thermal resistances between the working substance and the external heat reservoirs. Hence, finite-time thermodynamics will be chosen as a powerful tool to characterize the multi-irreversibilities in the real engine. For a given input rate of heat $\dot{q}_h$, when the irreversibility of finite-rate heat transfer and non-ideal regeneration in the heat engine are considered, the maximum efficiency can be expressed as [10]

$$\eta_{\text{engine}} = \frac{\dot{q}_h/K + (a - 1)T - aT_0 + T_e}{2aT + a[\dot{q}_h/K + (a - 1)T - aT_0 + T_e]}, \quad (6)$$

where $a = xC/[R \ln(V_2/V_1)]$ measures the irreversibility of finite-rate heat transfer in the heat engine, $T_e = \{[(a + 1)T + aT_0 - \dot{q}_h/K]^2 - 4a(a + 1)TT_0\}^{0.5}$, $K = k_1/[(1 + b)(1 + \sqrt{k_1/k_2})^2]$, x is the fractional deviation from ideal regeneration, b is the ratio of the time spent on the regenerative branches to that on the isothermal branches, C is the heat capacity of the working substance per mole partaking in the regenerative processes, k_1 and k_2 are respectively the thermal conductances between the working substance and the heat reservoirs at temperatures T (the temperature of exhaust gas from MCFC) and T_0 (ambient temperature).

As illustrated in Fig. 1, a part of the waste heat produced in the fuel cell is directly released as heat-leak to the environment [24], and this amount of the heat can be given by [15,16]

$$\dot{Q}_{\text{loss}} = \alpha A_1(T - T_0), \quad (7)$$

where α is the convective heat-leak coefficient, and A_1 denotes the effective heat-transfer area. Combined with the previous analysis, the rate of waste heat from the MCFC to the Stirling heat engine is given by

$$\begin{aligned}
\dot{q}_h &= -\Delta \dot{H} - P_{\text{cell}} - \dot{Q}_{\text{loss}} - \dot{Q}_{\text{re}} \\
&= -\frac{\Delta h}{n_e F} j A - U_{\text{cell}} j A - \alpha A_1(T - T_0) - k_{\text{re}}(1 - \varepsilon)(T - T_0). \quad (8)
\end{aligned}$$

By substituting Eq. (8) into Eq. (6), the optimum efficiency and power output of the Stirling heat engine may be respectively expressed as

$$\eta_{\text{engine}} = \frac{a_1(1 - \eta_{\text{cell}})j - (T - T_0)(a_2 + a_3) + (a - 1)T - aT_0 + T_e}{2aT + a[a_1(1 - \eta_{\text{cell}})j - (T - T_0)(a_2 + a_3) + (a - 1)T - aT_0 + T_e]} \quad (9)$$

and

$$P_{\text{engine}} = -\frac{A\Delta h}{a_1 n_e F} [a_1(1 - \eta_{\text{cell}})j - (T - T_0)(a_2 + a_3)] \times \frac{a_1(1 - \eta_{\text{cell}})j - (T - T_0)(a_2 + a_3) + (a - 1)T - aT_0 + T_e}{2aT + a[a_1(1 - \eta_{\text{cell}})j - (T - T_0)(a_2 + a_3) + (a - 1)T - aT_0 + T_e]}, \quad (10)$$

where $a_1 = -(A\Delta h)/(n_e FK)$ is a colligation measurement for the systemic structure, $a_2 = (\alpha A_1)/K$ and $a_3 = (k_{re}/K)(1 - \varepsilon)$ are two parameters used to characterize the influences of the heat-leak irreversibility from the fuel cell to the surroundings and non-perfect regeneration in the regenerator on the performance of the hybrid system.

2.4. The efficiency and power output of the hybrid system

It should be mentioned that the total thermal energy available in the system corresponds to the enthalpy change of the overall electrochemical reaction, i.e., $Q_{\text{all}} = -\Delta H$ [19]. By using equations (3), (4), (9) and (10), one may obtain the efficiency and the power output of the entire MCFC–Stirling engine hybrid system, i.e.,

$$\begin{aligned} \eta_{\text{hybrid}} &= \frac{P_{\text{hybrid}}}{\dot{Q}_{\text{all}}} = \frac{P_{\text{cell}} + P_{\text{engine}}}{-\Delta \dot{H}} \\ &= \eta_{\text{cell}} + \eta_{\text{engine}} \times \left[1 - \eta_{\text{cell}} - (T - T_0) \left(\frac{a_2}{a_1 j} + \frac{a_3}{a_1 j} \right) \right] \end{aligned} \quad (11)$$

and

$$\begin{aligned} P_{\text{hybrid}} &= \eta_{\text{hybrid}} (-\Delta \dot{H}) = -\frac{jA\Delta h}{n_e F} \left\{ \eta_{\text{cell}} + \eta_{\text{engine}} \right. \\ &\quad \times \left[1 - \eta_{\text{cell}} - (T - T_0) \left(\frac{a_2}{a_1 j} + \frac{a_3}{a_1 j} \right) \right] \left. \right\}. \end{aligned} \quad (12)$$

It is seen from equations (11) and (12) that the efficiency and the power output of hybrid system are larger than that of a sole MCFC, and the efficiency and power output are closely dependent on the irreversible losses including the irreversibilities within the fuel cell itself and originating from the heat transfer between the MCFC and Stirling heat engine. In the next section, the general performance characteristics and the optimal criteria of the hybrid system will be revealed.

3. General performance characteristics and optimal criteria

Optimal design and analysis of the hybrid system require a thorough understanding of its performance limitations. Equations (11) and (12) clearly show that the performance of the hybrid system depends on a set of thermodynamic and electrochemical parameters such as the fuel cell temperature (T), ambient temperature (T_0), operating current density (j), and the parameters related to the heat transfer between the MCFC and the Stirling heat engine

as well as the heat-leak to the surroundings, i.e., a , a_1 , a_2 and a_3 . In the following calculations, the anode gas composition is taken as 60% H_2 + 25% H_2O + 15% CO_2 , the cathode gas composition is given as 8% O_2 + 59% N_2 + 8% CO_2 + 25% H_2O , and the parameters $a = 0.01$, $a_1 = 0.103 \text{ K A}^{-1} \text{ m}^2$, $a_2 = 0.008$, $a_3 = 0.005$ are chosen. The related values of the input parameters not mentioned are summarized in Table 2 [5,7], and these parameters are kept constants unless mentioned specifically.

By using Eqs. (11) and (12), the efficiency and power density of the hybrid system for different current density are presented in Fig. 4, where $P^* = P/A$ is the power density. It can be clearly seen from Fig. 4 that both the efficiency and power density of the hybrid system first increase then decrease as the current density increases, and there exist a maximum efficiency η_{max} and a maximum power density P_{max}^* , where j_η and j_{P^*} are, respectively, the corresponding current densities at the maximum efficiency η_{max} and the maximum power density P_{max}^* . Compared with the efficiency and power density of a sole MCFC, the efficiency and power density of the hybrid system is significantly improved because waste heat in the fuel cell is utilized. Both the efficiency and the power density augment with the increase of current density when $j < j_\eta$, while they reduce with the increasing current density when $j > j_{P^*}$. It is obvious that the regions of $j < j_\eta$ and $j > j_{P^*}$ are not optimal from the thermodynamic viewpoint although the hybrid system may work in these regions. Hence, the optimal region of the current density should be located in

$$j_\eta \leq j \leq j_{P^*}. \quad (13)$$

Table 2
Parameters used in the modeling [5,7,9].

Parameter	Value
Operating pressure, p_0 (atm)	1
Operating temperature, T (K)	893.15
Ambient temperature, T_0 (K)	293.15
Activation energy of anode, $E_{\text{act,an}}$ (J mol $^{-1}$)	53,500
Activation energy of cathode, $E_{\text{act,cat}}$ (J mol $^{-1}$)	77,300
Partial pressure of H_2 in the anode, $p_{\text{H}_2,\text{an}}$ (atm)	0.6
Partial pressure of CO_2 in the anode, $p_{\text{CO}_2,\text{an}}$ (atm)	0.15
Partial pressure of H_2O in the anode, $p_{\text{H}_2\text{O},\text{an}}$ (atm)	0.25
Partial pressure of O_2 in the cathode, $p_{\text{O}_2,\text{cat}}$ (atm)	0.08
Partial pressure of N_2 in the cathode, $p_{\text{N}_2,\text{cat}}$ (atm)	0.59
Partial pressure of CO_2 in the cathode, $p_{\text{CO}_2,\text{cat}}$ (atm)	0.08
Partial pressure of H_2O in the cathode, $p_{\text{H}_2\text{O},\text{cat}}$ (atm)	0.25
Faraday constant, F (C mol $^{-1}$)	96,485
Number of electrons, n_e	2
Universal gas constant, R (J mol $^{-1}$ K $^{-1}$)	8.314

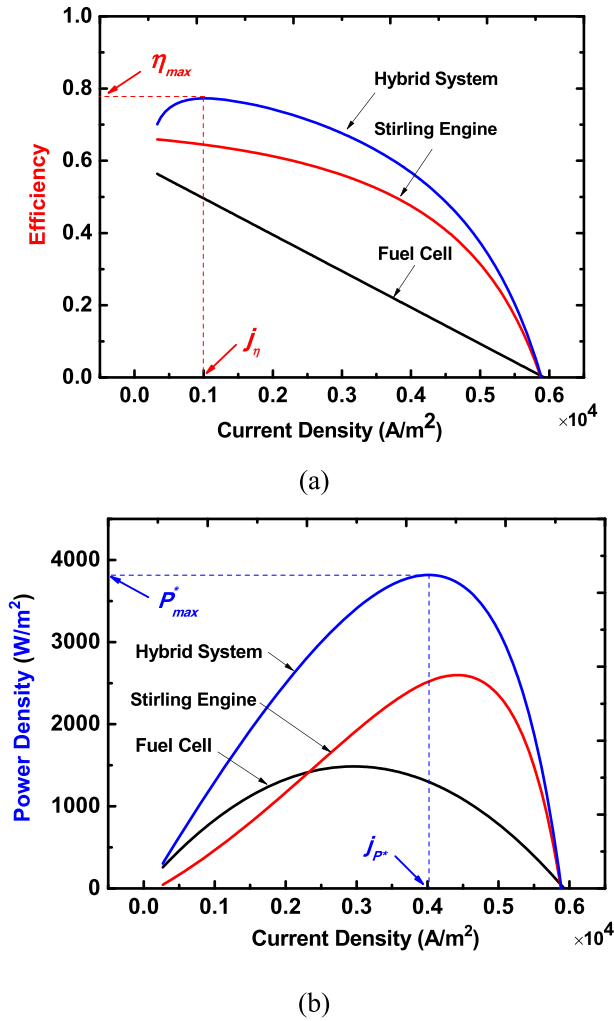


Fig. 4. The curves of (a) the efficiency, and (b) the power density varying with the current density, where $P_{hybrid}^* = P_{hybrid}/A$ is the power density, j_{η} and j_{P^*} are the current densities at maximum efficiency η_{max} and maximum power density P_{max}^* , respectively.

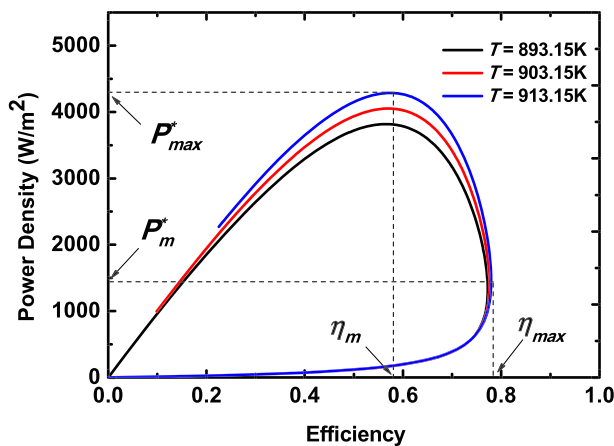


Fig. 5. The curves of the power density varying with the efficiency at different operating temperature.

It shows that j_{η} and j_{P^*} determine the lower and upper bounds of the optimized current density, respectively. In the practical operation of the MCFC–Stirling heat engine hybrid system, engineers should choose a reasonable current density according to Eq. (13) to ensure that the system is operated in the optimal region.

Fig. 5 shows the power density versus the efficiency at different operating temperatures, where P_m^* and η_m are the power density at the maximum efficiency η_{max} and the efficiency at the maximum power output P_{max}^* , respectively. According to Fig. 5, one can determine the optimally operating region, which has a negative slope in the part of the η – P^* curve. When the hybrid system operates in this region, the power density will decrease as the efficiency increase, and vice versa. Thus, the optimal ranges of the efficiency and power density are given as

$$\eta_{max} \geq \eta \geq \eta_m \quad (14)$$

and

$$P_m^* \leq P^* \leq P_{max}^*, \quad (15)$$

respectively.

The above results show that P_m^* , η_m , P_{max}^* and η_{max} are the four important parameters of the MCFC–Stirling heat engine hybrid system, where P_m^* and η_m determine the allowable optimum values of the lower bounds of the power density and efficiency, while P_{max}^* and η_{max} determine allowable optimum values of the upper bounds. It is significant to note that the four important parameters closely depend on the thermodynamic and electrochemical parameters of the hybrid system and can be calculated numerically for the given values of other parameters.

4. Discussion

It is noteworthy that the developed system model can be used to investigate the effect of the various operating conditions on the performance of the hybrid system. In this section, a parametric analysis is carried out based on the performance criteria for the variation of operating conditions to characterize the system behavior.

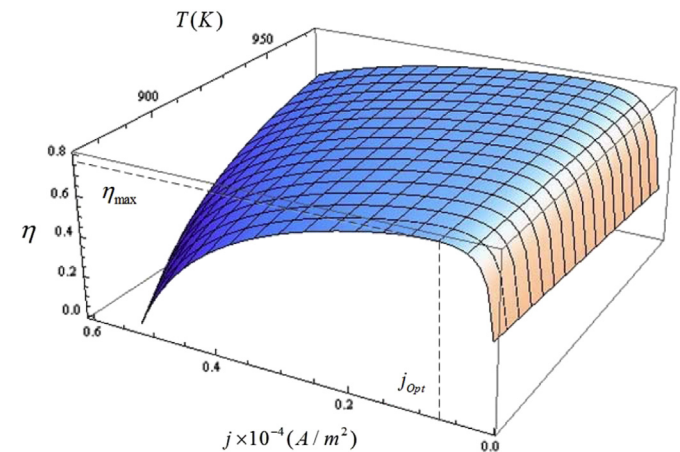


Fig. 6. The three-dimensional curve of the efficiency varying with the current density and temperature, where the values of parameters are listed in Table 1. The system efficiency will increase with the rise of the operating temperature, meanwhile, the maximum efficiency and the corresponding current density will also be slightly increased as the operating temperature is increased.

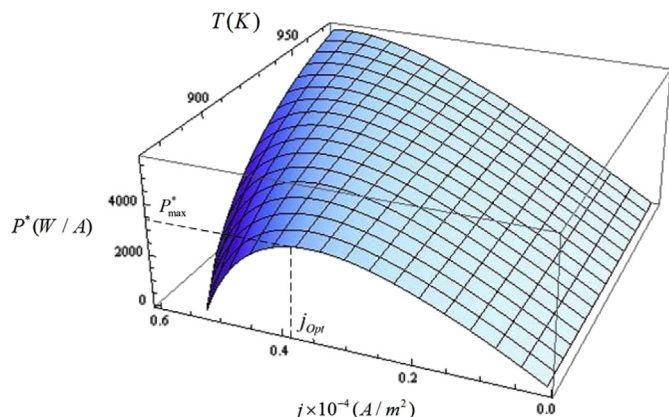


Fig. 7. The three-dimensional curve of the power density varying with the current density and temperature, where the values of the relevant parameters are the same as those used in Fig. 6. The system power density will increase with the rise of the operating temperature, meanwhile, the maximum power density and the corresponding current density will also be slightly increased as the operating temperature is increased.

4.1. The effects of the operating conditions

As indicated by Eqs. (11) and (12), the performance of hybrid system is closely related to a various of operating conditions such as temperatures, partial pressures of anode or cathode, and operating pressures. Next, the influences of both the operating temperature T and the hybrid system inlet temperature of the reactants T_i on the performance of the system will be discussed respectively. The operating temperature of the system is an important parameter because it directly affects the various overpotentials of the fuel cell as well as the performance of the heat engine. The power density and efficiency of the MCFC–Stirling heat engine hybrid system operating at a temperature range of 873–973 K and a current density range of 0–6000 A m^{−2} are presented in Figs. 6 and 7, where the ambient temperature $T_0 = 298.15$ K is chosen. As shown in Figs. 6 and 7,

the system performance will also increase with the rise of the operating temperature. Meanwhile, the maximum efficiency, maximum power density, and the corresponding current densities will also be slightly increased as the operating temperature is increased. Generally, the hybrid system inlet temperature of the reactants T_i is often higher than that of the ambience T_0 because the reactants are supplied to the system as being highly compressed, and T_i is assumed to be equal to the ambient temperature T_0 when the reactants are provided at 1 ambient pressure [12]. The low stack inlet temperature of reactants may drop the operating temperature of the stack and the lower operating temperature will also deteriorate the performance of the hybrid system, thus, it is easy to predict that the performance of the hybrid system will be improved as the temperature T is increased or as the temperature T_i is elevated. In addition, for the problem how to select the operating temperature of the system, one may simultaneously consider the investment cost and the degradation issue involved in manufacturing both a stack with the required thermal stability as well as the whole system that can be operated at that specified temperature.

It is well-known that the performance of hybrid system will be strongly affected by the different partial pressures of gases in anode and cathode, as shown in Fig. 8. It is seen from Fig. 8 that the different partial pressure of H₂ and H₂O at the anode will result in power increasing and efficiency declining, or conversely. However, with the partial pressures of O₂ and CO₂ at the cathode increasing, both the efficiency and the power density are improved. This may be explained as follow: the concentration increase of O₂ and CO₂ will result in a higher chemical reaction rate, which results in a net increase in the performance.

Additionally, gas operating pressure can also exert great influence on the performance of the system. As illustrated in Fig. 9, the greater the operating pressure, the better the performance is. However, the increase in the operating pressure must be at the expense of the additional electrical energy consumption. Hence, the reasonable selection of the operating pressure is very important in the actual operation of hybrid system. The larger the operating pressure, the smaller the distance between molecules is, and accordingly, the chemical reaction rate will be strengthened at larger operating pressure conditions. In essence, the method by raising the operating pressure to improve the performance is the same as that by increasing the reactant composition.

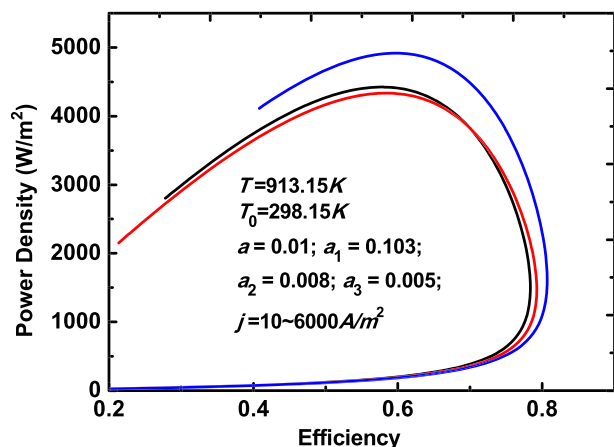


Fig. 8. The curves of the power density varying with the efficiency for different partial pressures of gases in anode and cathode, where the meanings of the curve color are as follows: black line (50%H₂ + 5%CO₂ + 45%H₂O)_{an} + (8%O₂ + 8%CO₂ + 25%H₂O + 59%N₂)_{cat}, red line (80%H₂ + 5%CO₂ + 15%H₂O)_{an} + (8%O₂ + 8%CO₂ + 25%H₂O + 59%N₂)_{cat}, blue line (80%H₂ + 5%CO₂ + 15%H₂O)_{an} + (16%O₂ + 16%CO₂ + 20%H₂O + 48%N₂)_{cat}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

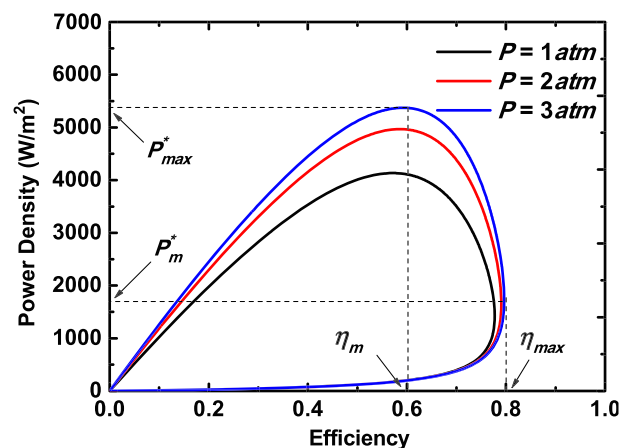


Fig. 9. The curves of the power density varying with the efficiency at different pressure conditions.

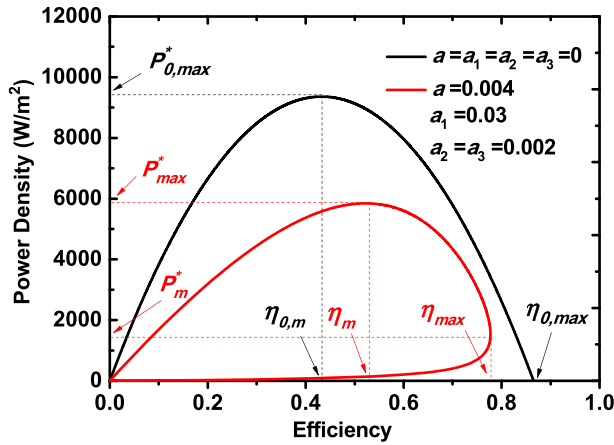


Fig. 10. The curves of the power density varying with the efficiency at different parameters a, a_1, a_2 and a_3 , where the black line represents the upper bound of performance.

4.2. The upper bound of the performance

It is interesting to wonder what the upper bound of performance for the hybrid system is. When the Stirling heat engine is reversible, the heat leak losses of the MCFC and the regenerative losses of the regenerator are negligible, i.e. $a = a_1 = a_2 = a_3 = 0$, Eqs. (11) and (12) can be, respectively, reduced to

$$\eta = \eta_{cell} + \left(1 - \frac{T_0}{T}\right)(1 - \eta_{cell}) \quad (16)$$

and

$$P = -\frac{jA\Delta h}{n_e F} \left[\eta_{cell} + \left(1 - \frac{T_0}{T}\right)(1 - \eta_{cell}) \right]. \quad (17)$$

As shown in Fig. 10, the black line represents the scope of the performance, where $P_{0,max}^*$ and $\eta_{0,max}$ are respectively the maximum power density and maximum efficiency that the hybrid system can be possibly reached, $\eta_{0,m}$ is the efficiency corresponding to $P_{0,max}^*$. When the different values of the parameters a, a_1, a_2, a_3 are chosen, the performance bounds of the system will be different, the black line in Fig. 10 represents the performance limit for the hybrid system.

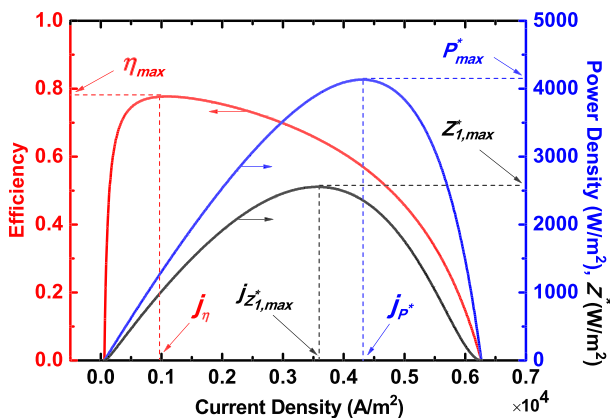


Fig. 11. The curves of the efficiency, power density, and multi-objective function varying with the current density, where $Z^* = Z/A$, $j_{Z_{1,max}^*}$ is the current density corresponding to $Z_{1,max}^*$.

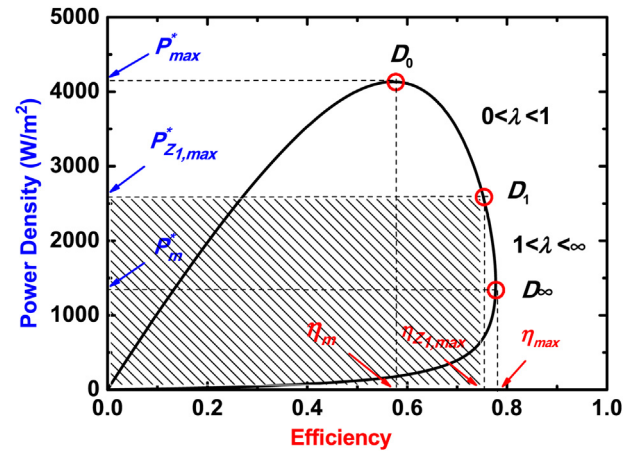


Fig. 12. The $P^*-\eta$ curve used to expound the physical meaning of the multi-objective function, where $\eta_{Z_{1,max}^*}$ and $P_{Z_{1,max}^*}^*$ are, respectively, the efficiency and power density corresponding to $Z_{1,max}^*$.

4.3. The multi-objective optimization

Suffered by the limit of performance bounds, engineers should choose some reasonable operating conditions in order to improve the system performance. Due to the different optimization objectives such as the efficiency and power density are coupled or affected one another through operating conditions, the multi-objective optimization technologies are often used [25–27]. For this reason, one may introduce a new multi-objective function which is defined as the product of the efficiency with a weighting factor and power output [5], i.e.,

$$Z_\lambda = \eta^\lambda P, \quad (18)$$

where λ is a weighting factor, whose value is determined by the practical requirements for the power output and the efficiency. In other words, the multi-objective function is a concrete value of the hybrid system, and $0 \leq \lambda < \infty$. If one focus more on the efficiency than power output, the weighting factor should be located in $1 < \lambda < \infty$. When $\lambda \rightarrow \infty$, the multi-objective function may be rewritten as a new form, i.e. $Z_\lambda^{1/\lambda} = \eta P^{1/\lambda}$, which is efficiency. If one takes more attention to the power output, the weighting factor should be located in $0 \leq \lambda < 1$. When $\lambda = 0$, the multi-objective function may become one objective function, i.e., $Z_0 = P$. If an engineer gives the same attention to the power output and the efficiency, the weighting factor can be chosen as $\lambda = 1$, which has been shown in Fig. 11.

In order to discuss the choice problem of the optimal current density, we will mark some important points in Fig. 12, which illustrates more clearly how to select the optimal operating region. Points D_0, D_1 and D_∞ on the curve, respectively, correspond to the state that Z_λ^* attains its maximum when $\lambda = 0, 1$ and ∞ . Point D_λ represents any point on the $\eta-P^*$ curve between D_0 and D_∞ . The horizontal and vertical coordinates corresponding to D_λ may form a rectangle, whose area is just equal to Z_λ^* . In Fig. 12, the area of the shaded part is equal to $Z_{1,max}^*$, where the power output and efficiency are equally treated.

It is clearly seen from Fig. 12 that the weighting factor λ plays an important role in the multi-objective function. The optimal operation region $i_\eta \leq i \leq i_{P^*}$ can be subdivided according to the different requirements for both the efficiency and the power output. If one emphasizes more on the efficiency than on the power output, the

optimal operation region of the current density, power output and the efficiency, respectively, should be

$$j_{\eta} \leq j \leq j_{Z_{1,\max}}, \quad (19)$$

$$\eta_{\max} \geq \eta \geq \eta_{Z_{1,\max}} \quad (20)$$

and

$$P_m^* \leq P^* \leq P_{Z_{1,\max}}^*. \quad (21)$$

If more attention is paid on the power output than on the efficiency, the optimal operation regions of the parameters mentioned above are, respectively, determined by

$$j_{\eta} \leq j \leq j_{P^*}, \quad (22)$$

$$\eta_{Z_{1,\max}} \geq \eta \geq \eta_m \quad (23)$$

and

$$P_{Z_{1,\max}}^* \leq P^* \leq P_{\max}^*. \quad (24)$$

5. Conclusions

The importance of the present paper lies in a new cycle model which can describe the general characteristic of MCFC–Stirling heat engine hybrid system. The various irreversible thermodynamic and electrochemical losses are identified and the individual effect of these irreversibilities to the hybrid system is investigated through parametric study. It is found that the performance of the MCFC can be greatly enhanced by using a Stirling heat engine for further power generation. The upper and lower bounds of the efficiency and power output are determined for the whole system through numerical simulations. Moreover, the effects of some operating conditions such as the operating temperature, partial pressures of gases in anode and cathode and operating pressure on the performance of the hybrid system are illustrated. The problem how to give consideration to the efficiency and power output in the optimal region of the current density is discussed in detail. The results obtained here may provide some theoretical basis for the optimal design and operation of practical MCFC–Stirling heat engine hybrid system. This method may be easily extended to other fuel cell hybrid system to develop irreversible models suitable for the optimal energy-management strategies of fuel cell hybrids.

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